POLYCONDENSED AROMATIC COMPOUNDS (PCA) AND CARCINOGENS IN THE SHALE ASH OF CARBONACEOUS SPENT SHALE FROM RETORTING OF OIL SHALE OF THE GREEN RIVER FORMATION

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I. POTENTIAL OF A COMMERCIAL OIL SHALE INDUSTRY IN THE U.S.A.

Although there are large oil shale deposits outside of the United States (e.g. Manchuria, USSR, Brazil, etc.), the United States contains some of the largest deposits of oil shale considered to be most promising for potential oil shale production. Among the U.S. deposits, those found in Colorado, Utah and Wyoming (representing oil shale of the Green River Formation) are known to be the richest ones in the nation and are contained predominantly in three large basins: The Piceance Creed Basin in Colorado, the Uintah Basin in Utah and the Green River Basin in Wyoming. Among these the Colorado deposits are considered to be the richest in high grade oil shale.

The oil shale deposits occur beneath 25,000 square miles of land of which 17,000 square miles (11 million acres) are believed to contain oil shale of potential "commercial" value. The Green River Formation deposits include high grade shales (averaging 25 or more gallons of oil per ton of rock) representing about 600 billion barrels of oil and an additional 1,200 billion barrels in places of low grade oil shales (with an average yield of 15-20 gallons per ton). The total in-place reserves of equivalent shale oil in the Green River Formation is estimated to amount to more than three trillion barrels.

In addition to the actual oil shale there are large reserves of sodium minerals present in the Piceance Basin, particularly nahcolite ($NaHCO_3$), trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), halite (NaCl) and a sodium-aluminum mineral, dawsonite ($NaAl(OH)_3CO_3$), which occur in zones at greater depths of the basin (1800-2000 ft.).

Thus, oil shale represents a sizable portion of the nation's energy sources. While the development of these resources was hampered in the past by inadequate technologies and strong competition with domestic and foreign crude oils, the increasing demand of energy sources in general and the political situation of the present time in particular, have brought the possibilities of a commercial exploitation of these deposits into sharper focus. This appears evident from the announcement of some industrial companies such as Colony Development Corporation, Union Oil and

Occidental Oil to venture into commercial production and the more recently announced leasing of government-owned land to Gulf Oil and Standard Oil of Indiana.

Based on statements made by some of the companies interested in the commercial exploitation of the waste oil shale deposits it would appear that at present the state of the art in mining and processing technologies for oil shale have reached the stage to be potentially feasible for commercial application although some of the operations will require disposal areas and availability of considerable water resources.

A 50,000 barrel/day plant using surface retorting of shale averaging 30 gallons per ton will require 72,000 tons per day of raw shale as feed and will discard 61,000 tons per day of spent shale. Most mining of the shale will probably be done by the room-and-pillar method, with perhaps 10-15% being treated by open pit mining; strip mining is not being considered at the present time. Their possible contribution to an oil shale industry, however, must be considered.

The extraction of the oil from the oil shale, i.e. the so-called "retorting process" can (in principle) be carried out by "above-ground" retorting using oil shale mined by one of the afore-mentioned methods or by the so-called "in-situ" or in-place underground retorting of the oil shale deposits.

There are three basic "methods" for above-ground retorting. In each case the shale rock is heated to 900-1000^{o}F and the oil vapors obtained are removed and cooled to yield a semi-viscous liquid which is shale oil. The latter is subsequently upgraded to yield either a pipeline crude or various partially refined products (fuel oil, naphtha, etc.). The main processes of this type are the following:

1. Tosco II/Colony Retort
2. Vertical Retorts such as
    a. Union Rock Pump Retort
    b. Bureau of Mines Gas Combustion Retort
    c. Petrosix Externally-heated Retort, and
    d. Paraho Vertical-kiln Retort.

All but the Union retort use downward gravity flow of shale.

3. Lurgi Retort using fluidized bed.

The "in-situ" processing of oil shale is an attractive alternative to mining and above ground retorting. Its main advantage claimed is the elimination of the mining and kiln retorting, the elimination of the necessity of disposal of spent shale and large scale water requirements. However, in-situ retorting has not been technically or economically successful to date and requires considerably more research - although most recently Occidental Oil Company has announced that it has demonstrated successfully an in-situ method which according to the report may be developed within the near future. The shale oil obtained from the retorting of oil shale stems from the cracking of the organic matter contained in the marlstone type sedimentary rock of the oil shale. The major portion of this organic matter is an insoluble high molecular weight organic material called "kerogen." In the case of the oil shale of the Green River Formation kerogen represents a three-dimensional organic matrix composed of more complex cyclic organic subunits called "proto-kerogen" linked together by longer alkane or ether type compounds bridging these subunits. Entrapped within this matrix are residues of protokerogen components which have as yet not combined with each other by diagenesis due to increase in viscosity and the admixture of considerable amounts of inorganic mineral matter. The mixture of the two major components forms the rather compact rock called oil shale. Heating the rock (retorting) to 900-1200°C will break up the organic matrix and form lower molecular weight organic hydrocarbons which yield the major constituents of the shale oil produced.

The technology of oil shale mining and production in the United States and the economics of the energy requirements are such that a commercial industry is eminent. However, some of the processes will require considerable amounts of water for their operation and will also lead to disposal problems. The water requirements will vary with the process involved. For a typical 50,000 barrel/day plant the water consumed would be 20 acre feet/day which is about 3 barrels of water per barrel of shale oil produced. Some 45% of this water is used for wetting and compaction of the discarded spent shale, 25% for retorting and upgrading and 30% for mining, crushing, etc. All water diverted is eventually consumed in the process. A one million barrel/day operation would require approximately a total of 175,000 acre ft. of water per year.

Furthermore, the initiation of a commercial oil shale operation for instance in the Piceance Basin will also generate solid waste of considerable proportion. On the basis of evaluations made by government and industry the estimated amount of spent shale generated at the end of 1979 (i.e. only five years hence) will be approximately 183,000 tons per day or over 60 million tons per year and by 1987 when the production is considered to exceed one million barrels/day, the spent shale produced will be about 1,280,000 tons/day or approximately 420 million tons of spent shale per year. In some types of operations an estimated 50-60 percent of the retorted residue could be replaced into the mine and 40-50 percent will have to be disposed on the surface.

II. POTENTIAL ENVIRONMENTAL IMPACT

Because of the necessity of solid waste disposal encountered in some processes, the water requirements and the possible socio-economic implications such an industry may have, it is not surprising that the potential problems of environmental impact of commercial operations were raised by an ever-increasing environmental-conscious segment of the population. This led eventually to the compilation of a six-volume Environmental Impact Statement prepared by the U.S. Department of the Interior, the finalized form of which was published in 1973. This document covers practically every facet of potential environmental impacts which could ensue from commercial oil shale operations and countermeasures proposed, the effectiveness of which have been already demonstrated experimentally in pilot studies. However, in many other aspects the "Impact Statement" does not (and probably was not intended to) provide final solutions but rather outlines potential problems and can by necessity provide only guidelines to possible solutions because in many cases there just is as yet not available sufficient hard core experimental data. There exists therefore in many areas covered by the Impact Statement the need of experimental implementation and/or corroboration and of course this is also indicated in the document.

This appears to be certainly true with respect to some aspects of the problem areas with which the research program conducted under this NSF Grant is concerned, i.e. the potential environmental effects stemming from the generation and disposal of carbonaceous spent shale. The data obtained from these investigations are to be considered preliminary at the present and represent a mere point of departure. However, with the foreseeable development of actual larger scale demonstration plants (in the order of 50,000 barrels of oil per day) these investigations appear to be timely and hopefully may contribute some new experimental data useful for a better evaluation of the potential environmental problems. The basic philosophy of the present research program is therefore to investigate these problems experimentally (in cooperation with the industry and government agencies interested in shale oil production), and make the results of these investigations available to all interested private and other government organizations and also publish them in the open literature.

What then are the possible environmental impacts which could conceivably result from the generation and disposal of carbonaceous spent shale?

The major by-products from an oil shale operation are (a) the solid spent shale, (b) the process water generated during the retorting (pyrolysis) process and (c) process gases.

The composition and properties of the solid waste will depend on the type of retorting process used and the conditions of retorting. In some of the retorting processes the resulting spent shale still contains up to five percent carbon residue from the original organic matter present. This carbonaceous organic matter is in part present as organic compounds which are soluble in organic solvents. It stands to reason that due to the pyrolytic process used during retorting part of this organic matter consists of polycondensed organic matter (POM) which may include polynuclear or polycondensed aromatic hydrocarbons (PAH) and aza-azarines (AA) in addition to other types of higher moleculer weight organic compounds.

While in itself the formation of such compounds in small quantities is practically ubiquitous wherever pyrolysis of organic matter occurs and could therefore be regarded as more or less inconsequential, systematic and long range investigations carried out over the last few decades have shown that chronic exposure to certain polluting inorganic trace elements as well as trace amounts of polycondensed aromatic pollutants can have a detrimental effect on the ecology including man.

The fact that such organic compounds may be present (even in trace quantities) in carbonaceous spent oil shale cannot be overlooked for the simple reason of the magnitude of their production.

Obviously not every commercial operation will produce carbonaceous spent shale. However, there is considerable evidence that some of the processes ready for larger scale operations will produce carbonaceous spent shale. Consequently the disposal of this type of solid waste involves not only inorganic trace elements and water leachable salts but also considerable amounts of residual organic matter containing poly-condensed aromatic hydrocarbons.

On the basis of the estimated spent shale generated in 1979 alone, this could include up to 3.1 million tons of carbonaceous matter which may contain as much as 6,000 tons of solubilizable and in part volatile organic compounds. It is conceivable that even a small portion of these organic compounds may have (in the long run) some undesirable impact on the ecosystem because of potential leaching and accretion of this material in the aquifer, their potential concentration during recycling operation of impounded water and their possible translocation into the vegetation and/or partial transfer into the surrounding atmosphere. Some of this rational applies not only to above ground operations but alto to potential "in-situ" operations. The potential impact from these trace organic matter from carbonaceous spent shale has not been investigated to date systematically and in greater detail. It is the main objective of the present research program to fill this gap. The exposition of the more detailed potential problems involved, and methods of approach utilized, and the preliminary experimental results obtained to date are presented in the First Annual Report to be submitted to NSF and various other interested agencies.

III. PRELIMINARY RESULTS

The major activities and preliminary results of these investigations (carried out to date) can be summarized as follows:

A. Samples of soil, water, vegetation and air from various pristine (i.e. as yet undisturbed) areas of potential future oil shale operations were collected and analyzed for their content of polycyclic organic matter in particular polycondensed aromatic hydrocarbons including those of known carcinogenic properties such as 3,4 benzo[a]pyrene. This was done to establish a base line for future comparative studies.

B. Samples of carbonaceous spent shale from various retorting processes used in pilot plants (operated at various times) were collected and also analyzed for their content of polycondensed aromatic compounds.

Neither of the two studies mentioned above have as yet been completed and more detailed comparisons must await additional experimental data.

The results of these preliminary investigations indicate the following:

1. Carbonaceous spent shale with up to 5% organic carbon content, contains higher molecular weight and lower molecular weight organic material soluble in organic solvents. The benzene soluble fraction ranges from 0.02 to 0.2 percent, depending on the retorting conditions and the age of the spent shale.

2. The benzene soluble portion contains polynuclear organic matter (POM) such as polycyclic aromatic hydrocarbons (PAH) and aza-azarines. The PAH compounds contain (among other components) also 3,4 benzo[a]pyrene.

3. The percent amount of benzene soluble material in carbonaceous s pent shale is about one order of magnitude higher than in the soils from pristine areas but about one order of magnitude lower than that found in airborne particulate matter,e.g. collected in industrial areas. However, on a volume basis (cubic meter of material) spent shale is higher in soluble material (12 order of magnitudes).

4. In a traverse of a gulch projected as a disposal area the extractable material in soil is in general also one order of magnitude lower than in the spent shale ash, but varies with the density of vegetation growing at the particular sampling site; this is due to the fact that endogenic PAH compounds generated by the vegetation will evnntually end up in the soil.

5. The content of benzo[a]pyrene in the benzene extracts is about three order of magnitude higher than that in the extracts of soil and/or plant material from the pristine environment and 3 to 30 fold as high as in vegetables (e.g. salad with approximately 10 micrograms/kg dry weight) and smoked food (1-10 micrograms/kg dry weight).

6. Preliminary data also indicate that saline water from leached carbonaceous shale may be at least three to four order of magnitudes higher in PAH content than ground water or surface water from pristine areas.

7. Polycyclic aromatic compounds can apparently be leached from the carbonaceous spent shale by water to a considerable extent in the presence of water soluble inorganic salts.

8. Whether the amount of PAH compounds with known carcinogenic properties present in carbonaceous spent shale constitutes a serious hazard to the environment will need more extensive studies and additional experimental data to allow comparison with urban and industrial environments to which man is exposed at the present time. Therefore the final answers will have to await forthcoming results from extended investigations.

9. Studies on the oxidation of carbonaceous shale ash have been initiated. There are as yet not sufficient data available to lead to any definite conclusions.